Research Article

Paloma Roldán Del Cerro, Henriikka Teittinen, Isabella Norrbo, Mika Lastusaari, Jonathan Massera*, and Laeticia Petit

# Novel borosilicate bioactive scaffolds with persistent luminescence

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**Abstract:** Persistent luminescent amorphous borosilicate scaffolds were successfully prepared, for the first time, with a porosity of >70% using the burn-off technique. The persistent luminescence was obtained by adding the $SrAl_2O_4$:$Eu^{2+}$,$Dy^{3+}$ microparticles: i) in the glass melt or ii) in the glass crushed into powder prior to the sintering. The scaffolds prepared by adding the microparticles in the glass melt exhibits lower persistent luminescence and a slower reaction rate in simulated body fluid than the scaffolds prepared by adding the microparticles in the glass powder due to the release of strontium from the microparticles into the glass during the glass melting.

**Keywords:** borosilicate glasses, $SrAl_2O_4$:$Eu^{2+}$,$Dy^{3+}$ microparticles, persistent luminescence, scaffold, in-vitro testing, direct particle doping method

## 1 Introduction

Lindfors *et al*. reported that bioactive glass particles dissolution was incomplete even 14 years post-surgery although the in-vitro study predicted the complete dissolution of the glass [1]. This clearly showed the importance of following the materials reaction, in-vivo and in real time. Persistent luminescent (PeL) materials have become, in the past years, an important class of functional materials [2] finding application in optical bioimaging among other. PeL refers to the type of emission that lasts from seconds to hours, after the removal of the irradiation source [3]. The combination of glass materials and persistent luminescent particles has great potential for breakthrough in light-based technology for the medical field allowing a better understanding of the glass reaction in-vivo through bioimaging. However, despite the great potential of these new composites, their studies have been limited. The main reason lies in the challenges in precipitating persistent luminescent crystals within a glassy matrix. Glass ceramics which contain a glassy phase and $Eu^{2+}$,$Dy^{3+}$-doped $SrAl_2O_4$ persistent luminescence particles have been fabricated using the so called "Frozen sorbet method" by Nakanishi *et al.* [4]. However, with this technique, the glass composition should not only precipitate a PeL crystal but also nucleate those crystals in the bulk materials rather than at the surface, in order to have good crystals dispersion. Later, PeL phosphate-based bioactive glasses were successfully obtained by adding PeL microparticles (MPs) in the glass batch prior to the melting [5–7]. However, this melting process could not be used to prepare PeL silicate glasses due to their high glass melting temperature at which the MPs are not thermally stable. Therefore, the melting process was modified; PeL bioactive borosilicate glasses could be obtained by adding the PeL MPs in the glass melt prior to quenching the glass [8].

Due to their architectural structure, porous scaffolds have been of great interest especially for bone healing processes [9]. To be considered as good candidates, the scaffold must possess specific properties [10]: they must be biocompatible and permit cell adhesion, normal functioning of the cell and cell migration. After implantation, the scaffold must also present negligible immune reaction to reduce inflammatory response. Additionally, the scaffolds should degrade and disappear with time as they are not permanent implants. Finally, the scaffold should have a porous three-dimensional (3D) architecture with interconnected pore structure [9]. Recently, it was found that

***Corresponding Author: Jonathan Massera:** Tampere University, Faculty of Medicine and Health Technology, Korkeakoulunkatu 3, 33720, Tampere, Finland; Email: jonathan.massera@tuni.fi
**Paloma Roldán Del Cerro, Laeticia Petit:** Photonics Laboratory, Tampere University FI-33101 Tampere, Finland
**Henriikka Teittinen:** Tampere University, Faculty of Medicine and Health Technology, Korkeakoulunkatu 3, 33720, Tampere, Finland
**Isabella Norrbo:** University of Turku, Department of Chemistry, Vatselankatu 2, 20014 Turku, Finland; Doctoral Programme in Physical and Chemical Sciences, University of Turku Graduate School (UTUGS), Turku, Finland
**Mika Lastusaari:** University of Turku, Department of Chemistry, Vatselankatu 2, 20014 Turku, Finland; Turku University Center for Materials and Surfaces (MatSurf), Turku, Finland

borosilicate glass can be sintered into 3D porous scaffolds allowing good bioactivity [11, 12]. However, these scaffolds do not exhibit spectroscopic properties to allow one to track in-vivo the bioresponse of the scaffold.

We present, for the first time to the best of our knowledge, the preparation and the in-vitro testing of borosilicate bioactive scaffolds with PeL properties. The preparation of the PeL scaffolds is first presented. The in-vitro testing was performed by immersing the scaffolds in simulated body fluid (SBF). Their dissolution was assessed by ICP-OES. The change in the PeL was investigated as a function of the immersion time in SBF.

## 2 Material and methods

Borosilicate glass scaffolds, with the composition $26.93SiO_2$-$26.93B_2O_3$-$22.66Na_2O$-$1.72P_2O_5$-$21.77CaO$ (in mol%), were prepared with persistent luminescence using the burn-off technique. The persistent luminescence of the scaffolds was obtained by adding 2 wgt% of commercial persistent luminescent microparticles (MPs) with the composition $SrAl_2O_4$:$Eu^{2+}$,$Dy^{3+}$ (Jinan G.L. New Materials, China, BG-01) in the glass. The raw materials used to prepare the glass were $SiO_2$ (Umicore, 99.99%), and $Na_2CO_3$ (Honeywell, >99.5%), $H_3BO_3$ (Sigma Aldrich, >99.5%), $CaCO_3$ (Alfa Aesar, 99%), and $CaHPO_4{\cdot}2H_2O$ (Sigma Aldrich, 98%).

Two techniques were used to prepare the persistent luminescent scaffolds. The MPs were added in the glass melt as in [8]: the glass was first melted at 1250°C for 30 min and then the temperature of the melt was reduced to 950°C for the addition of the $SrAl_2O_4$:$Eu^{2+}$, $Dy^{3+}$ MPs. The MPs containing glass was then quenched 3 min after adding the MPs and finally annealed at 400°C, during 6 h to remove the residual stress from the quench. After annealing, the glass was crushed and sieved to a particle size <38μm to favor flow sintering and densification [11]. The glass to porogen ($NH_4(HCO_3)$) ratio was 30/70 in volume. The glass powder and porogen were mixed, pressed into pellets at 25 MPa and sintered at 300°C for 5h and finally at 555°C for 1h. The scaffolds prepared using this technique are labeled "MPs-containing glasses".

The other technique used to prepare the persistent luminescent scaffolds was to melt the glass at 1250°C for 30 min. After annealing at 400°C for 6 h, the glass was crushed and sieved to a particle size <38μm. The MPs were mixed with the glass powder in a mortar until uniform distribution of the MPs in the glass powder as checked from an uniform green persistent luminescence from the MPs-glass powder mixture. As for the other scaffold, the glass to porogen ($NH_4(HCO_3)$) ratio was 30/70 in volume and the mixture was pressed at 25 MPa and finally sintered at 300°C for 5h and finally at 555°C for 1h. The scaffolds prepared with this technique are labeled "addition of MPs in the glass powder".

A scanning electron microscope (Carl Zeiss Crossbeam 540) equipped with Oxford Instruments X-Max$^N$ 80 EDS detector was used to image and analyze the composition of the samples. The samples were coated with a thin carbon layer before EDS mapping. The accuracy of the elemental analysis was ± 1.5 mol%.

The persistent luminescence (PeL) spectra were measured at room temperature using a Varian Cary Eclipse Fluorescence Spectrophotometer equipped with a Hamamatsu R928 photomultiplier (PMT). The samples were irradiated for 5 min at room temperature with a compact UV lamp (UVGL-25, 4 W, $\lambda_{exc}$: 254 nm) and the spectra were measured 1 min after ceasing the irradiation using a data collection time of 4 s for the whole spectrum. The photoluminescence (PL) spectra were measured using a CCD camera (Avantes, AvaSpec-HS-TEC) ($\lambda_{exc}$: 266 nm, Nd:YAG pulse laser, 8 ns, TII Lotis).

The in-vitro testing was performed in simulated body fluid (SBF) [13]. The pH was adjusted to 7.4 at 37°C. The PeL scaffolds were immersed in SBF for 24h, 48h, 72h, 1 week and 2 weeks at 37°C in an incubating shaker (100 RPM). The SBF volume to mass of scaffold ratio was kept constant at 10ml/100mg in all experiments. After every immersion, the pH was measured and 1 ml of the immersion solution was diluted in 9 ml of 1M $HNO_3$ for ICP-OES (ICP-OES 5110, Agilent technology) analysis. In order to perform the in-vitro testing, 12 scaffolds for each series were prepared.

## 3 Results and discussion

The scaffolds were obtained using the burn-off technique by adding PeL microparticles (2wgt%) during the melting (scaffold labeled as MPs-containing glasses) and also in glass powder (scaffold labeled as addition of MPs in the glass powder). The porosity of all the scaffolds was measured at (72 ± 2) %. As seen in Figure 1, no sharp peaks are seen in the XRD pattern of the scaffold prepared from the MPs-containing glasses. However, the XRD pattern of the scaffold obtained by adding the MPs in the glass powder prior to the sintering exhibits few peaks which are similar to those of the MPs alone. Therefore, no or little amount of other crystals than the MPs are expected in the glass matrix confirming that the sintering process did not lead to

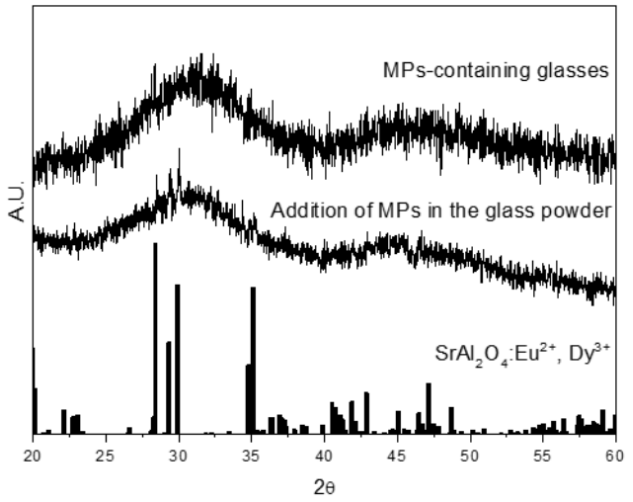


**Figure 1:** XRD pattern of the scaffolds and of the MPs alone

the crystallization of the glass matrix. Therefore, the sintering process is thought to be optimized to prepare scaffolds with an appropriate porosity required for bone tissue engineering.

As explained in [8], the MPs are expected to be corroded when added in the glass melt. Therefore, in agreement with the absence of peaks in the XRD pattern of the scaffolds prepared from MPs-containing glass, a lower amount of MPs are expected in the scaffolds prepared from the MPs-containing glass than in the scaffolds prepared by adding the MPs in the glass powder. Nonetheless, despite some corrosion of the MPs, when introduce in the glass melts, in all cases the PeL properties of the remaining particles is not found to be greatly impacted. No inhomogeneity in the intensity of the PeL within each scaffold and between the scaffolds from the same series was detected confirming the homogeneous dispersion of the MPs inside each scaffold and between the scaffolds.

The PeL and PL spectra of the investigated scaffolds are presented in Figure 2a and 2b, respectively.

The PeL spectra exhibit a band at 520 nm which is due to the $4f^6 5d^1 \rightarrow 4f^7$ transition in $Eu^{2+}$ [4]. One can notice that the scaffolds (MPs in the glass powder) exhibit a stronger PeL than the scaffolds (MPs-containing glasses). The normalized PL spectra of the scaffolds (Figure 2b) exhibit a band at 532 nm, which is the harmonic of the excitation and also a band centered at 525 nm with a shoulder at ~425 nm, which can be associated to the $4f^6 5d^1 \rightarrow 4f^7$ emission from $Eu^{2+}$ located in two different cation sites in the $SrAl_2O_4$ structure [14]. Additional bands at ~590 and 615nm, not present in the PL spectra of the MPs alone, are seen in the PL spectra of the scaffolds prepared from the MPs-containing glass. These bands are related to the emission from $Eu^{3+}$ ions [7]. As explained in [8], the MPs are expected to be corroded during the melting leading to the diffusion of the MPs elements to the glasses, including $Eu^{2+}$ which are suspected to be oxidized into $Eu^{3+}$ when diffusing in the glass. It should be pointed out that no changes in the PL spectra (not shown here) were observed at each step of the fabrication of the scaffold for both scaffolds indicating that the fabrication process has no impact on the $Eu^{2+}$ site and on the formation of $Eu^{3+}$.

The bioactive response of the scaffolds was tested using SBF. The scaffolds were immersed in SBF for 2 weeks. The PeL spectra of the scaffolds are presented in Figure 3a and 3b.

Upon immersion in SBF, a decrease in the PeL intensity can be detected. A similar reduction in the PeL intensity of sintered bodies upon immersion in SBF was reported in [15] and was related to the mineralization of the sintered bodies. Therefore, it is shown here that the scaffolds with appropriate porosity and persistent luminescence can be used to track the bioresponse of the glass overtime.

The mass loss of the scaffolds and the pH of the solution as a function of immersion time are presented in Figures 4a and 4b, respectively.

The mass loss, which can be related to the dissolution rate, increases with immersion time in SBF. Although the scaffolds have the same composition, the initial mass loss of the scaffolds prepared by adding the MPs in the glass powder is the fastest indicating that this scaffold possesses a faster dissolution rate than the scaffold prepared from MPs-containing glass. One should point out that after 2 weeks in SBF, the mass loss is similar for both scaffolds. As seen in Figure 4b, the pH increases upon immersion in SBF. This can be related to the release of alkaline and alkaline earth ions from the glass to the solution increasing the basicity of the solution as explained in [15, 16]. The initial increase in pH is faster when immersing the scaffold prepared by adding the MPs in the glass powder than the scaffold prepared from MPs-containing glass. One can observe that after 2 weeks, the pH of solution containing the scaffold prepared by adding the MPs in the glass powder is slightly higher than for solutions containing the scaffolds prepared from MPs-containing glass.

The Figure 5 presents the Si (a), B (b), Ca (c), P (d) and Sr (e) concentration upon immersion time in SBF.

Upon immersion in SBF, Si, B, and Ca are released into the solution confirming the progressive dissolution of the scaffolds in SBF in agreement with the increase in the mass loss (Figure 4a) and in the SBF pH overtime (Figure 4b). As expected, the scaffold prepared from the MPs-containing glass exhibits a slower initial dissolution rate

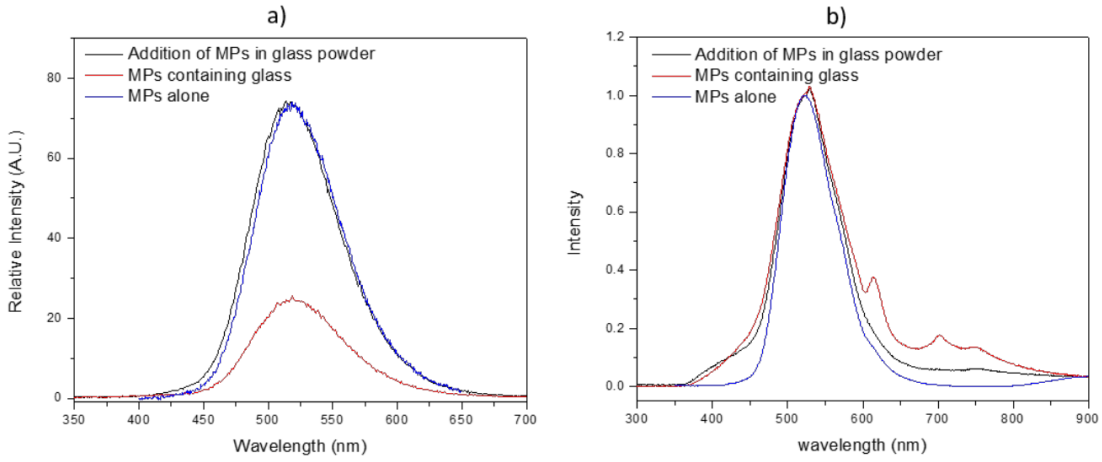


**Figure 2:** Persistent luminescence (PeL) (a) and normalized conventional luminescence (PL) (b) spectra of the scaffolds. Also shown are the spectra of the MPs alone (the PeL band was normalized to the PeL band of the scaffold prepared by adding the MPs in the glass powder)

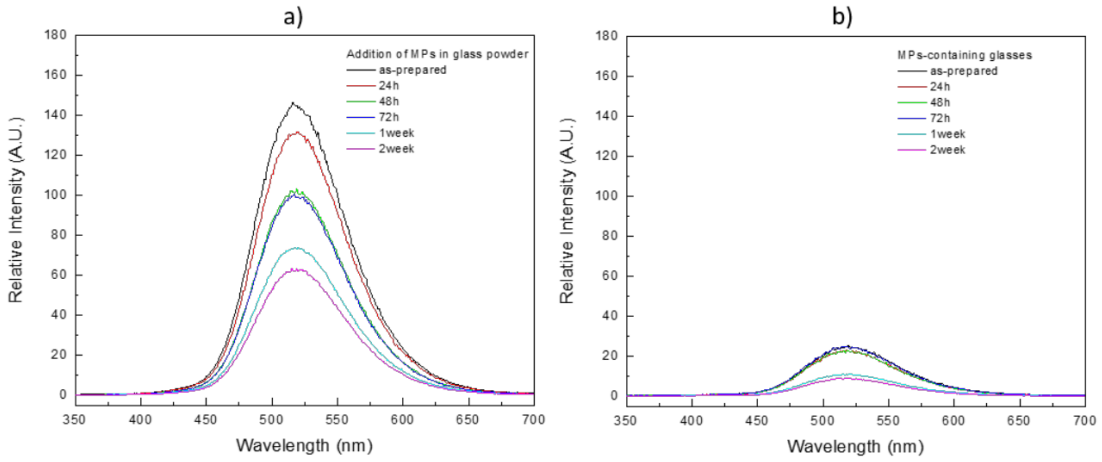


**Figure 3:** Persistent luminescence spectra of the scaffolds prepared by adding the MPs in the glass powder (a) and from MPs-containing glass (b)

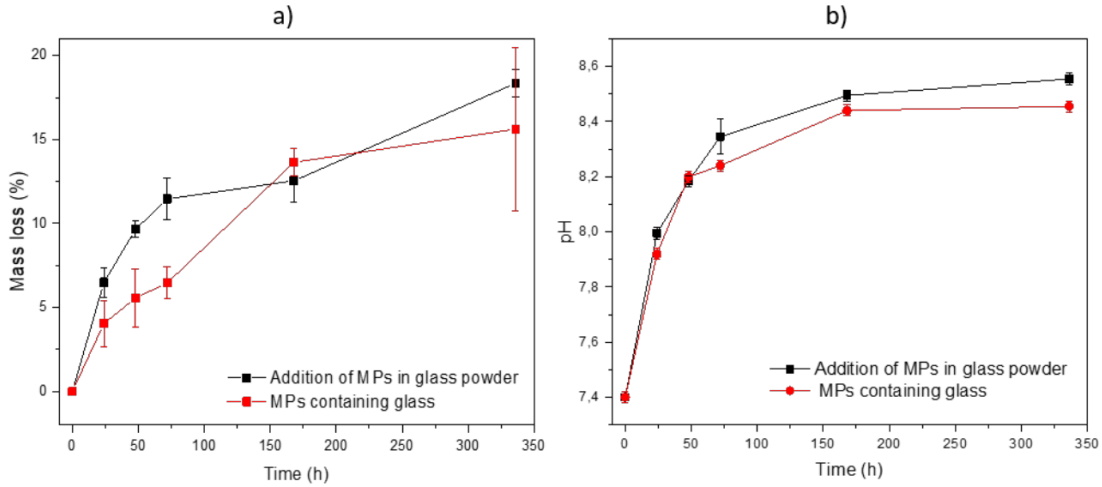


**Figure 4:** Mass loss of the scaffolds (a) and pH of the solution (b) as a function of time in SBF

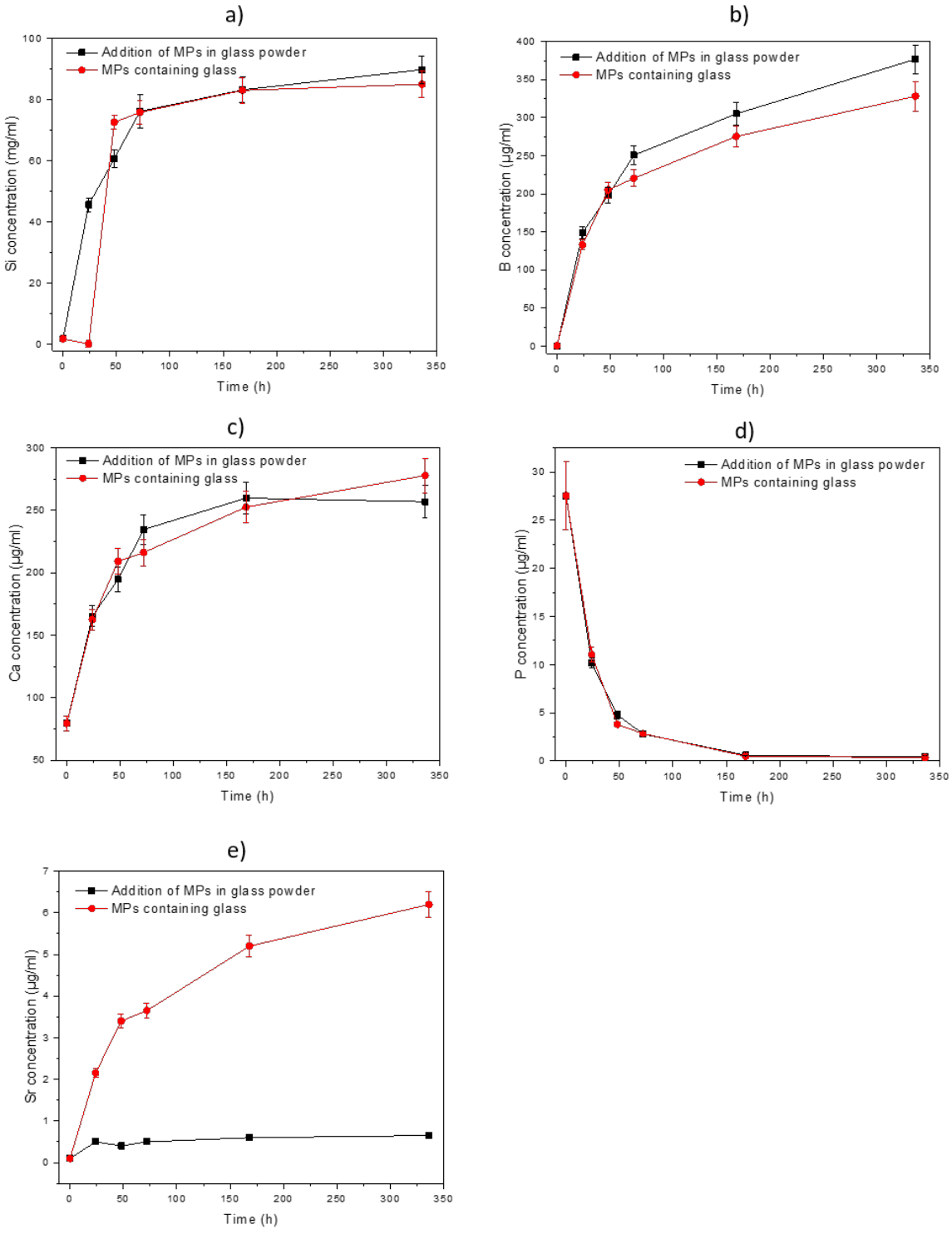


**Figure 5:** Ion concentration in the immersion solution of the scaffold for Si (a), B (b), Ca (c), P (d) and Sr (e) as a function of immersion time

than the other scaffold. As seen in Figure 4e, a high release of Sr was detected from the scaffold prepared from the MPs-containing glass. The high Sr content released in the solution can be related to the glass preparation. Indeed, as explained in [8], the MPs are suspected to decompose when added in the glass melt. The corrosion of the MPs by the glass melt leads to the diffusion of the MPs elements in the glass. Therefore, a large amount of Sr ions is suspected to leach out from the MPs to the glassy phase during the preparation of the glass which is then released when the scaffold is immersed in SBF. One should point out that the bioactivity of the S53P4 glass was found to be retarded when replacing CaO by SrO [17]. Therefore, it is possible that the dissolution rate of the investigated borosilicate glasses is reduced due to the presence of Sr ions in the glass matrix.

The decrease in P content (Figure 5d) is a sign of the precipitation of a Ca-P layer [12], which can be confirmed using FTIR. Figure 6 shows the IR spectra measured at the surface of the scaffolds prepared from the MPs-containing glass post immersion, taken as an example.

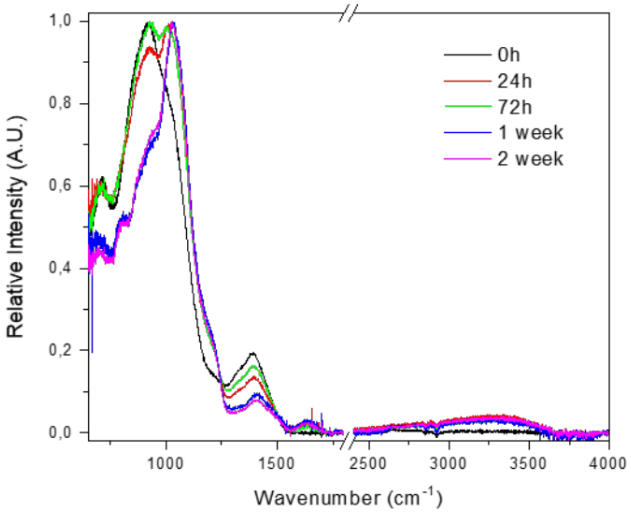


**Figure 6:** IR spectra of the scaffolds (MPs-containing glass) for up to 2 weeks in SBF

The IR spectra exhibit the same bands as those reported and analyzed in [18]. Upon immersion in SBF, the bands at 930 and 1380 $cm^{-1}$ decreases in intensity at the expense of the band at 1023 $cm^{-1}$. According to [18], these changes are a clear sign of the dissolution of the borate network and of the soluble silica from the glass as well as of the formation of the formation of the hydroxycarbonated apatite (HA) layer. Indeed, upon immersion, the main band shifts to 1019 $cm^{-1}$ and sharpens due to the appearance of the band at ~1030$cm^{-1}$ assigned to $\nu_{as}$(POP) vibration of $Q^2$ units in large rings [19]. The presence of PO is also evidenced by the bands at ~880$cm^{-1}$, assigned to P-O vibrations [20] and at ~960 $cm^{-1}$ attributed to the $\nu_{as}$(P-O-P) vibration of $Q^2$ units in small rings [19]. The shoulder at ~960 $cm^{-1}$ can also be assigned to C-O vibration modes in $CO_3^{2-}$, supported by the increase of the doublet in the 1350-1550$cm^{-1}$ region, typical of vibration from carbonate group, with increasing immersion time. The broad band in the 2750-3500 $cm^{-1}$ region, related to water absorption [21], increases in intensity with increasing immersion time in agreement with the formation of a HA layer on top of hydrated silica-rich layer. In summary, the presence of the bands related to OH, CO and PO vibrations confirms the formation of the HA layer at the surface of the scaffold which is a promising sign of bioactivity [17, 18]. Similar changes in the IR spectra upon immersion in SBF were recorded from the other scaffolds. It is the progressive reaction of the scaffolds with SBF, associated with the progressive glass dissolution and the formation of an amorphous CaP layer, which is thought to reduce the intensity of the PeL properties of the scaffolds.

As seen in Figure 7a and 7b, particles with an average size of ~25-50 µm were found, the composition of which was $SrAl_2O_4$ confirming that the MPs maintained their compositional integrity in their center and so their PeL and PL properties as discussed in the previous section.

Leaching of Al and Sr elements from the MPs to the glass can be seen in the scaffolds prepared from the MPs-containing glass. It is the leaching of these elements from the MPs which is thought to modify the site of the $Eu^{2+}$ and therefore to lead to low PeL intensity.

Glass particles can also be seen in Figures 7 and 8.

A layer with a thickness of ~5µm can be seen at the surface of the glass particles upon immersion in SBF. This layer is formed by 2 two distinct layers as seen in [12, 22]: the first layer is rich in Si while the outermost layer is rich in Ca and P with a Ca/P ratio ~1.61, close to HA, as typically reported in such bioactive glasses. Indeed, as reported in a thorough in-vitro dissolution and cell culture study, on both discs and extracts, upon dissolution/reaction of this glass (especially as particles) a HA layer forms at the glass surface [22]. The precipitation of HA is a first indication of the potential glass bioactivity. It is interesting to point-out that the precipitation of HA occurs also within the core of the scaffolds, and not only at the surface, which is an indication of pore size and interconnection promising for fluid, nutrient and mass transport.

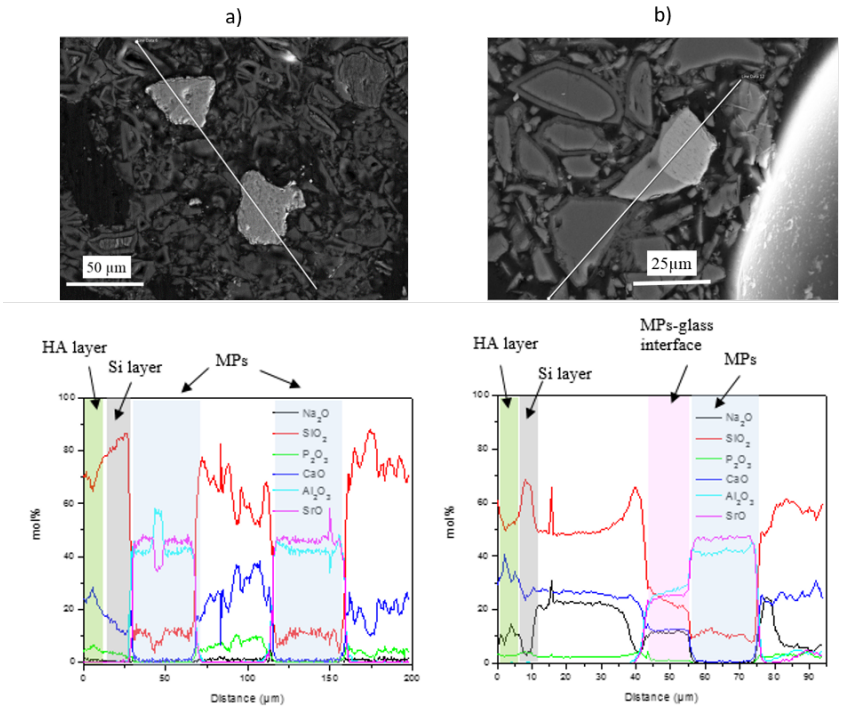


**Figure 7:** SEM/EDS line profiles giving the elemental distribution across the MP diameter and interface with the scaffold prepared by adding the MPs in the glass powder (a) and from the MPs-containing glass (b) after 2 weeks in SBF

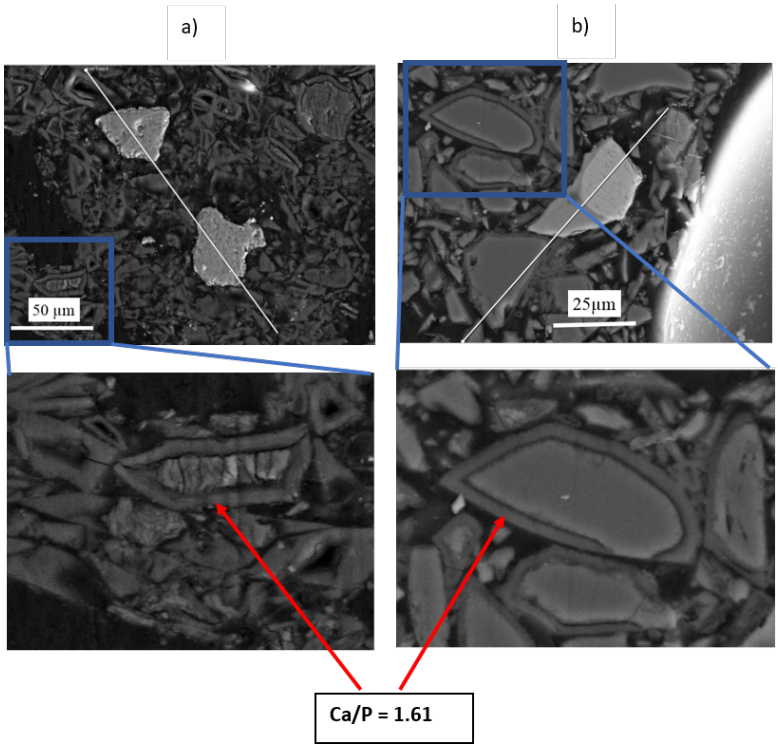


**Figure 8:** SEM images of the scaffolds prepared by adding the MPs in the glass powder (a) and from the MPs-containing glass (b) post immersion in SBF for 2 weeks in SBF

# 4 Conclusion

New PeL borosilicate scaffolds were prepared using the burn-off technique with a porosity of >70%. They exhibit PeL, the intensity of which decreases upon immersion in SBF while maintaining the amorphous nature of the construct. Upon immersion in SBF, a hydroxycarbonated apatite (HA) layer precipitates at the surface of the glass particles which is a promising sign of bioactivity. From the changes in pH of the SBF solution and the mass of the scaffolds, the scaffold prepared by adding the MPs in the glass melt exhibits a slower reaction rate than the scaffold prepared by adding the MP in the as-prepared glass crushed into powder. This difference in the dissolution rate is thought to be related to release of Sr from the MPs into the glass during the glass preparation.

We clearly show that the newly developed scaffolds can be used to track in-vivo implant mineralization, the progressive decrease in the persistent luminescence properties being related to the progressive mineralization overtime.

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**Ethical approval:** The conducted research is not related to either human or animals use.

**Conflict of Interests:** The authors declare no conflict of interest regarding the publication of this paper.

# References

[1] Lindfors N.C., Koski I., Heikkilä J. T., Mattila K., Aho A. J., A prospective randomized 14-year follow-up study of bioactive glass and autogenous bone as bone graft substitutes in benign bone tumors, J Biomed Mater Res B, 2010, 94B, 157-164.

[2] Brito H. F., Hölsä J., Laamanen T., Lastusaari M., Malkamäki M., Rodrigues L. C. V., Persistent luminescence fading in $Sr_2MgSi_2O_7:Eu^{2+},R^{3+}$ materials: a thermoluminescence study, Opt. Mater. Express, 2012, 2, 287-293.

[3] Aitasalo T., Hölsä J., Jungner H., Lastusaari M., Niittykoski J., Thermoluminescence Study of Persistent Luminescence Materials: $Eu^{2+}$- and $R^{3+}$-Doped Calcium Aluminates, $CaAl_2O_4:Eu^{2+},R^{3+}$, J Phys Chem B, 2006, 110 (10), 4589-4598.

[4] Nakanishi T., Katayama Y, Ueda J, Honma T, Tanabe S., Komatsu T., Fabrication of Eu:$SrAl_2O_4$-based glass ceramics using frozen sorbet method, J Ceram Soc JPN, 2011, 119, 609-615.

[5] Massera J., Głuchowski P., Lastusaari M., Rodrigues L.C.V., Petit L., Hölsä J., Hupa L., Hupa M., New alternative route for the preparation of phosphate glasses with persistent luminescence, J. Eur. Ceram., 2015, 35, 1255.

[6] Massera J., Gaussiran M., Głuchowski P., Lastusaari M., Hupa L., Petit L., Processing and characterization of new phosphate glasses containing $CaAl_2O_4:Eu^{2+},Nd^{3+}$ and $SrAl_2O_4:Eu^{2+},Dy^{3+}$ microparticles, J. Eur. Ceram., 2015, 35, 3863-3871.

[7] Massera J., Gaussiran M., Gluchowski P., Lastusaari M., Petit L., Hölsä J., Hupa L., Effect of the glass melting condition on the processing of phosphate-based glass-ceramics with persistent luminescence properties, Opt. Mater, 2016, 52, 56-61.

[8] Roldán Del Cerro P., Salminen T., Lastusaari M., Petit L., Persistent luminescent borosilicate glasses using direct particles doping method, Scr. Mater., 2018, 151, 38-41.

[9] Jones J., Hench L.L., Regeneration of trabecular bone using porous ceramics, Curr. Opin. Solid State Mater. Sci., 2003, 7 (4), 301-307.

[10] Hutmacher D. W., Scaffolds in tissue engineering bone and cartilage, Biomaterials, 2000, 21(24), 2529-2543.

[11] Erasmus E.P., Johnson O. T., Sigalas I., Massera J., Effects of Sintering Temperature on Crystallization and Fabrication of Porous Bioactive Glass Scaffolds for Bone Regeneration Sci. Rep., 2017, 7, 6046.

[12] Erasmus E.P., Johnson O. T., Massera J., Sigalas I., In vitro Evaluation of Porous borosilicate, borophosphate and phosphate Bioactive Glasses Scaffolds fabricated using Foaming Agent for Bone Regeneration, Sci. Rep., 2018, 8, 3699.

[13] Kokubo T., Kushitani H., Sakka S., Kitsugi T., Yamamuro T., Solutions able to reproduce in vivo surface-structure changes in bioactive glass-ceramic A-$W^3$, J. Biomed. Mater. Res., 1990, 24, 721-734.

[14] Aitasalo T., Hölsä J., Jungner H., Krupa J-C., Lastusaari M., Legendziewicz J., Niittykoski J., Annihilation of the persistent luminescence of $MAl_2O_4:Eu^{2+}$ by $Sm^{3+}$ co-doping, Radiat. Meas., 2004, 38, 727-730.

[15] Saarinen M., Nommeots-Nomm A., Hokka M., Laurila J., Norrbo I., Lastusaari M., Massera J., Petit L.,. Persistent Luminescent Particles Containing Bioactive Glasses: Prospect Toward Tracking in-vivo Implant Mineralization using Biophotonic ceramics, J. Eur. Ceram., 2018, 38, 287-295.

[16] Huang W., Rahaman M. N., Day D.E., Li Y., Mechanisms for converting bioactive silicate, borate, and borosilicate glasses to hydroxyapatite in dilute phosphate solution, Phys & Chemistry of Glasses: Eur. J. Sci. Technol. B. 2006, 47, 1-12 .

[17] Massera J., Hupa L., Influence of SrO substitution for CaO on the properties of bioactive glass S53P4, J Mater Sci Mater Med, 2014, 25 (3), 657-668.

[18] Fabert M., Ojha N., Erasmus E., Hannula M., Hokka M., Hyttinen J., Rocherullé J., Sigalas I., Massera J., Crystallization and sintering of borosilicate bioactive glasses for application in tissue engineering, J. Mater. Chem. B, 2017, 5 (23), 4514-4525.

[19] Wilder J.A., Shelby J.E., Property Variation in Alkali Alkaline-Earth Metaphosphate Glasses, J. Am. Ceram. Soc., 1984, 67(6), 438-444.

[20] Konidakis I., Varsamis C.-P.E., Kamitsos E.I., Möncke D., Ehrt D., Structure and Properties of Mixed Strontium-Manganese Metaphosphate Glasses, J. Phys. Chem., 2010, 114, 9125-9138.

[21] McMillan P.F., Remmele R.L., Hydroxyl sites in $SiO_2$ glass: A note on infrared and Raman spectra, Am. Mineral, 1986, 71, 772-778.
[22] Ojansivu M., Mishra A., Vanhatupa S., Juntunen M., Larionova A., Massera J., Miettinen S., The effect of S53P4-based borosilicate glasses and glass dissolution products on the osteogenic commitment of human adipose stem cells, PlosOne, 2018, 13, e0202740.